Letters to the Editor

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ULTRAVIOLET ABSORPTION OF CARBONATE AND BICARBONATE IONS

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Carbonate and bicarbonate ions have planar structure and D_{3h} symmetry (Mooney, 1932) similar to that of nitrate ion and hence are expected to give rise to absorption spectra similar to nitrate ion (Mookherji and Tandon, 1962; Tandon, 1961). However, a detailed study (Janz and Mikawa, 1960) of the correlation of 0-0 repulsion force constant and separation distances, reveals that though there is a close resemblance between the structures of nitrate and carbonate ions yet they differ in charge distribution. There is positive charge on nitrogen atom in close proximity to the negative charge on the nitrate ion (Tandon, 1962), while carbon atom in carbonate ion has no charge. Due to these differences in charge distribution and values of atomic orbitals the energies of the absorption bands of nitrate and carbonate ions should not be the same, though the general nature of the spectrum be similar as demanded by close resemblance in structure. Hence the authors with improved technique made a close study of the spectrum with a "Uvispek" spectrophotometer scanning the spectrum at an interval of 2.5 Å in the region 1850 Å to 3600 Å. Aqueous solutions at different concentrations of several carbonates and bicarbonates showed one weak band at about 2000 Å and the other, very weak compared to the first, at about 2700 Å. The band at 2000 Å was observed earlier by Ley and Arends (1932) but not the band at 2700 Å.

X-ray (Mooney, 1932), infrared (Ramdas, 1953) and magnetic studies (Mookherji, 1951) showed that the presence of hydrogen bond in bicarbonate ion

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does not affect the carbonate group. Consequently, the absorption spectra of carbonates and bicarbonates should be similar. This is what has been observed.

The band width of both the bands is almost the same and $\sim 10^3$ cm $^{-1}$ which is nearly the same as that of the nitrate ion. Hence it is inferred that the excited states for both the bands may be antibonding (Jorgensen, 1962).

The oscillator strength P for 2000 Å band was calculated following Jorgensen (1954) which comes out $\sim 10^{-4}$. This compares well with that of 3000 Å band of nitrate ion, suggesting that the transition is not an allowed one. The other band at 2700 Å has an oscillator strength $\sim 10^{-6}$, characteristic of a highly forbidden transition. Transition probabilities calculated following Tanabe and Sugano (1954) and Mookherji and Tandon (1962) for both the bands also lead to the same conclusion.

The band at 2000 Å showed fine structure but could not be studied closely because of poor intensity. Work is in progress in that direction in our laboratory, with improved procedure.

The shift of this band towards shorter wavelengths (blue shift) with progressive dilution, the feeble intensity ($P \sim 10^{-4}$) and the resemblance of the structure with nitrate ion suggest a $n \rightarrow \pi^*$ transition. This is in conformity with the findings of the polar solvent's influences on the absorption frequency (McConnell, 1952).

Calculations by LCAO-MO treatment of carbonate ion similar to that of of nitrate ion by McEwen (1961) show that $n \rightarrow \sigma^*$ transition has energy smaller than $n \rightarrow \pi^*$ one. Thus low energy and intensity of the band at 2700 Å suggest that the band may be assigned to the forbidden $n \rightarrow \sigma^*$ transition. This is further supported by the large band width of the same order as that of 2000 Å band revealing the antibonding character of the orbital giving rise to the excited state.

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